

Interlayer Magnetic Frustration in Quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$

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Susceptibility, high-field magnetization and submillimeter wave electron spin resonance measurements of layered quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ are reported and compared to isomorphous NaNiO_2 . A new mechanism of magnetic frustration induced by the excess Ni ions always present in the Li layers is proposed. We finally comment on the possible realization of an orbital liquid state in this controversial compound.

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Since its synthesis in 1958 by Goodenough et al. [1], LiNiO_2 is a subject of continuous debate. Its ideal structure can be described as a packing of Li and NiO_2 slabs built up of edge sharing NiO_6 octahedra. Therefore, magnetic Ni and nonmagnetic Li hexagonal planes alternate along the $[111]_c$ direction, giving rise to a quasi-2D magnetic lattice. Detailed chemistry analysis of this compound has been motivated by its potential application in rechargeable batteries; this allowed to overcome the initial disagreement between results from different groups due to the sensitivity of the physical properties to the sample preparation method. On the other hand, theoretical interest on this system comes from the interplay between different degrees of freedom : doubly degeneracy of the Ni^{3+} ($t_{2g}^6 e_g^1$) orbitals and their eventual coupling to the $S=1/2$ spins, the effect of frustration in the triangular Ni lattice, the elusive nature of the magnetic interactions. In spite of numerous studies and significant progress on these subjects [2], the puzzling absence of both orbital and magnetic ordering, indeed clearly observed in isomorphous NaNiO_2 [3,4], remains a mystery. More recently, LiNiO_2 has been considered as the first realization of a quantum spin orbital liquid [5–8].

Here we report new measurements on well characterized homogeneous $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$. We study three samples, one of them being, to our knowledge, the closest one to stoichiometry reported up to now, and we compare their behavior to NaNiO_2 . The overall results agree with recent theoretical development [9] concerning the decoupling of the orbital and spin degrees of freedom, particular to these frustrated Jahn-Teller (JT) systems, and the always ferromagnetic (FM) sign of the intralayer Ni-Ni magnetic interactions. They also confirm the cluster model that we have proposed [10] to describe the

dependence on the concentration x of different properties. Furthermore, we can conclude that most probably stoichiometric LiNiO_2 does not exist, and that the clusters formed around the excess Ni ions on Li planes are responsible for the peculiar behavior of this system. In fact, when the intrinsic weak antiferromagnetic (AF) interaction between adjacent Ni layers, neglected in previous theoretical works [9,10], is taken into account, the effective FM coupling induced by those clusters frustrates the AF stacking of the FM Ni planes, hindering the long range 3D-magnetic ordering observed in NaNiO_2 below 20K [4].

The detailed description of the synthesis conditions and of the structural characterization of our NaNiO_2 and $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ samples has been given elsewhere [4,11]. The amount of extra Ni ions were determined by Rietveld refinement : $x=0.004$, 0.016 and 0.060 (± 0.002) in the latter system. The magnetic susceptibility measurements were performed on a SQUID magnetometer under 1mT field, between 2 and 300K using pressed pellets. High magnetic fields up to 23T were obtained using resistive magnets. Electron spin resonance (ESR) measurements were carried out at different frequencies and temperatures, using Gunn oscillators and Carcinotrons. The magnetic field (up to 12T) was produced by a superconducting magnet.

Fig. 1 reports the temperature dependence of the susceptibility M/H at 1mT, showing the high quality of our $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ sample, $x=0.004$. The curve presents a cusp around $T_\chi=7.5\text{K}$ when heating after zero field cooling (ZFC), whereas on field cooling (FC) M/H remains almost constant below T_χ . This is a typical spin-glass like behaviour. The inverse susceptibility H/M , shown in the inset of Fig. 1, can be fitted with a Curie-Weiss law between 70 and 300K, with an effective moment $\mu_{eff}=2\mu_B$ and a Weiss temperature $\theta=+26\text{K}$. These results are similar to those of Yamaura et al. [12] with $T_\chi=8.5\text{K}$, $\mu_{eff}=1.91\mu_B$ and $\theta=+29.5\text{K}$. The positive sign of θ indicates the predominance of FM interactions and the effective moment corresponds unambiguously to the low spin state ($t_{2g}^6 e_g^1$) of Ni^{3+} with $S=1/2$. It is interesting to point out that, the most stoichiometric sample has the lowest Weiss temperature, the linear dependence of $\theta(x)$ for $x \rightarrow 0$, precising the concentration determined from Rietveld analysis [11]. This allows us to say that our $x \simeq 0.004$ sample is the most diluted reported to date.

The existence of a well defined susceptibility peak is an indication of the homogeneity of the sample. Besides, if the Ni^{2+} ions were not distributed at random in the Li layers, this would lead to ferrimagnetic domains and to an additional anomaly at $\sim 240\text{K}$ in the susceptibility (only for mT fields).

Fig. 2 shows the magnetization at 4K of NaNiO_2 and $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ samples. The low field curvature, signature of ferrimagnetic clusters, vanishes when $x \rightarrow 0$, approaching the linear behavior observed [4] for the A-type antiferromagnet NaNiO_2 . For this compound, the saturation is reached at 10T and the moment $1\mu_B/\text{Ni}$ agrees again with the low spin state of Ni^{3+} . For the $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ samples the saturation is almost achieved at 23T with $M_{\text{Sat}} = (1-x)\mu(\text{Ni}^{3+})$. The Ni^{2+} moments are not involved in the latter formula since, they are still AF coupled, even at 23T, following the Goodenough-Kanamori-Anderson (GKA) rules (Ni^{2+} -O- Ni^{3+} form 180° bonds) [10]. The high field dependence of the magnetization of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ samples confirms the presence of extra AF interactions, compared to NaNiO_2 . Thus, the evolution of the magnetization curve with concentration x comes from ferrimagnetic clusters, created by these extra Ni^{2+} ions inducing AF couplings. Also the Arrot's plots at various temperatures in Ref. [11] are typical of an AF like NaNiO_2 . In fact, the small number of clusters for this x cannot explain by itself such macroscopic AF behaviour, strongly suggesting that, also in this case, there is an intrinsic weak AF interaction between adjacent Ni layers, $\sim 1\text{K}$ in NaNiO_2 [4].

Two different ESR studies have been already performed on diluted $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$. Ohta et al. [13], by measurements between 1.8 and 256K, up to 370GHz with pulsed magnetic fields, have shown the existence of two lines, already present at 86K, which split progressively with further cooling. At 1.8K, the frequency vs. magnetic field diagram suggested the existence of an internal field, since the extrapolated lines did not cross the origin. Barra et al. [14] have performed similar ESR measurements at 73 and 246GHz, interpreting the splitting of these two lines, observed below 130K, in terms of anisotropic g factors with $g_\perp \neq g_\parallel$. Then, they proposed a dynamical JT effect of the Ni^{3+} ions, which becomes static below 130K. Since $g_\perp \neq g_\parallel$, the occupied orbital should be $|d_{x^2-y^2}\rangle$, in contradiction with the EXAFS study by Rougier et al. [15]. In fact, these authors have shown the existence of elongated octahedra from 300K, i.e. a local JT effect, favoring the occupation of the $|d_{3z^2-r^2}\rangle$ orbital, as for isomorphous NaNiO_2 . In order to clarify this point we have undertaken a complete ESR study of the most stoichiometric sample, up to 285GHz at various temperatures. A typical low-temperature spectra is shown in the inset of Fig. 3. The signal is strongly anisotropic with the splitting discussed above, showing striking analogies with NaNiO_2 (Figs.8 and 9 in Ref. [3]). The frequency evolution at 50K of these two features,

called A and B, are presented in Fig. 3. The extrapolated lines cross the frequency axis at $3\pm 1\text{GHz}$, -1 ± 1 , for A and B respectively, confirming the existence of an internal field and invalidating the static-dynamical JT analysis. Such similar phenomenon in both, the Na and Ni compounds, indicates that the splitting of the ESR lines at low-temperature is not due to the JT effect but has a magnetic origin. We correlate this effect with the deviation from the Curie-Weiss law, observed below 70K for our most diluted sample (inset Fig. 1).

Fig. 4 shows the qualitative different ESR spectra of quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ compared to NaNiO_2 at $T=200\text{K}$, a temperature half lower than the temperature at which the JT distortion takes place for NaNiO_2 ($T_{JT} \simeq 480\text{K}$). Even at the high frequencies (230-285GHz) necessary to clearly separate the two g components in NaNiO_2 , there is now a single isotropic line around $g=2.17$. We will come back to this result.

In $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ there are only 90° Ni-O-Ni paths within the same plane, while Ni^{2+} ions in the Li planes introduce 180° Ni-O-Ni bonds. Considering the GKA rules and fitting the high temperature susceptibility as a function of the concentration x by a mean-field approach, we have shown [10] that the intralayer interactions are FM and the Ni-O-Ni couplings induced by the extra Ni in Li layers are AF. Moreover, in order to obtain a good description of the whole data, it was necessary to take into account that the intralayer Ni^{3+} -O- Ni^{2+} (Ni^{2+} ions in the Ni layers due to charge compensation) coupling J_{F1} is stronger than the Ni^{3+} -O- Ni^{3+} J_{F2} one. Though, ferrimagnetic cluster are formed : each Ni^{2+} ion in the Li plane connects 6 FM Ni ions (since the AF 180° Ni-O-Ni coupling applies twice), i.e. 3 in each of the two adjacent Ni layers. If also we consider the FM J_{F1} between Ni^{2+} and Ni^{3+} in the same Ni layer, then for $x=1/12$ homogeneously distributed excess Ni^{2+} ions, all sites are coupled. This percolation threshold appears to be in agreement with experiments (see Fig. 2 in Ref. [10]).

Since both intralayer interactions are FM, frustrated AF models in the triangular Ni layer, yielding a spin liquid [16–18] are inappropriate for this system. Other works [5–8,19] proposed LiNiO_2 as an example of a quantum orbital spin liquid, to explain both the absence of magnetic and orbital ordering. All these models assume a strong coupling between the orbital and spin degrees of freedom [so-called Kugel-Khomskii (KK) systems [20]]. Surprisingly, no author comments the EXAFS results by Rougier et al. [15] showing the existence of two different Ni-O distances in quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, with 4 short and 2 long Ni-O bonds, as in NaNiO_2 . Even if there is no macroscopic structural transition, this elongation of the NiO_6 octahedra occurs even at room temperature, and the local JT effect of the Ni^{3+} ions appears as the relevant process for the breakdown of orbital degeneracy. The KK rules concern cubic lattices with 180° bonds, and conclusions for these frustrated JT systems

are different [9]. In fact, as we have first point out [10], at 90°, and independently of the orbital e_g occupation, the intralayer magnetic Ni-Ni coupling is always FM.

According to the experimental results and theoretical considerations discussed above, we propose here a new mechanism of magnetic frustration in diluted $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$. The pure compound LiNiO_2 , if it exists would have the magnetic structure of NaNiO_2 . The magnetization, susceptibility and ESR measurements clearly show that the magnetic properties of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ approach those of NaNiO_2 when the excess Ni concentration $x \rightarrow 0$. At low temperature, the weak AF interplane Ni-O-Li-O-Ni interaction of the NaNiO_2 type [4] should lead to an AF macroscopic order (AF alternation of adjacent FM Ni planes), in agreement with Arrott's plots and magnetization curves. However, it seems that the smaller size of the Li ions does not allow the perfect stacking of the Na-Ni layers, and that a Ni concentration $x \neq 0$ always goes into the Li layers, inducing effective interplane Ni-Ni local FM couplings. Such competition of interactions leads to magnetic frustration, prevents the stabilization of long range ordering, and explains the spin glass behaviour observed in quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ at low temperature, without the necessity of evoking a spin liquid state. Fig. 5 shows a sketch of this frustration mechanism. Assuming that spins around a cluster turn progressively like a magnetic wall, to finally adopt the AF stacking of NaNiO_2 , an estimation of the number of perturbed spins by each additional Ni ion can be made. To simplify, in the case of an uniaxial crystal, the characteristic wall length writes

$$\delta_0 = a \sqrt{\frac{8H_E}{3H_A}} \quad (1)$$

where a is the cell parameter, H_E and H_A are the exchange and anisotropic fields, respectively [21]. Taking the characteristic field values obtained [4] for NaNiO_2 , yields $\delta_0 = 6a$. In our hexagonal symmetry, up to sixth-neighbor spins are perturbed, i.e. ~ 60 spins per cluster. Therefore, less than 1% of excess Ni in the Li planes can induce complete magnetic disorder in $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$.

EXAFS data indicate a JT elongation of the NiO_6 octahedra [15], but this effect remains local : there is no macroscopic structural transition. It is noteworthy that the isotropic ESR line at 200K is not necessary in contradiction with EXAFS. For instance, a configuration with elongated octahedra in orthogonal directions $|d_{3z^2-r^2} >$, $|d_{3x^2-r^2} >$, $|d_{3y^2-r^2} >$ could explain both data. On the other hand, recent theoretical work [9] proposed that the high degeneracy of mean-field orbital ground state in the frustrated Ni lattice is lifted by quantum orbital fluctuations (Villain's order by disorder), which select particular ferro-orbital states, as observed in NaNiO_2 . Then a weaker electron-lattice coupling, not enough for the stabilization of that ferro-orbital state, or even stronger

orbital fluctuations going against it, were invoked to explain the absence of a cooperative JT effect in LiNiO_2 .

Finally, we would like to point out that the susceptibility anomaly at $T_{of} \simeq 400\text{K}$ reported by Reynaud et al. [19], below which they claim that an orbitally frustrated state is established, is very weak and within the experimental error ($\Delta\chi \sim 3 \times 10^{-5} \text{cm}^3/\text{mol}$). Therefore, up to now, only the absence of a macroscopic structural distortion and the isotropic shape of the ESR line (Fig. 4) are indications of this complicate orbital state. Orbitals are much more difficult to measure than spins, and it will be a delicate task to distinguish between ordered chains in orthogonal directions, disordered or fluctuating orbitals. In any case this will not influence the magnetic behavior, that can be independently explained by the new frustration mechanism of Fig. 5. Small angle neutron measurements are in progress, in order to "see" these ferrimagnetic clusters.

In conclusion, from low and high magnetic field and ESR measurements on homogeneous quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, we have shown that the extra Ni ions always present in the Li planes, induce magnetic frustration in the low x limit, and this can explain the unusual magnetic properties. We have shown that the splitting of the ESR lines below the temperature at which the susceptibility deviates from the Curie-Weiss law, has a magnetic origin. The single isotropic ESR line above this temperature, together with EXAFS data, indicate a peculiar orbital occupation with elongated octahedra.

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FIG. 1. Temperature dependence of M/H at 1mT for $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, $x=0.004$. The open and full circles correspond to measurements on FC and on ZFC, respectively. Inset: H/M vs. T at 1mT for the same sample; the continuous line shows the Curie-Weiss law.

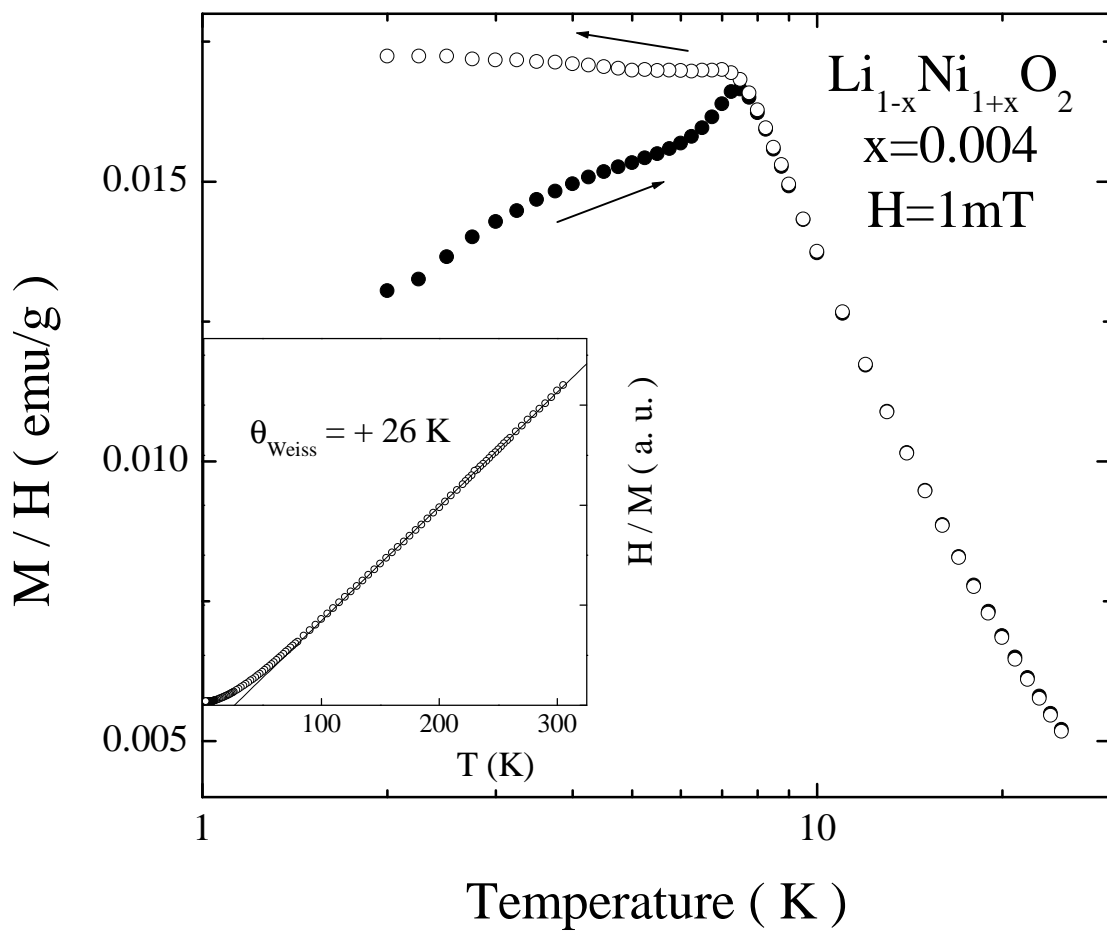
FIG. 2. Magnetization up to 23T of NaNiO_2 and various quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ samples at 4K.

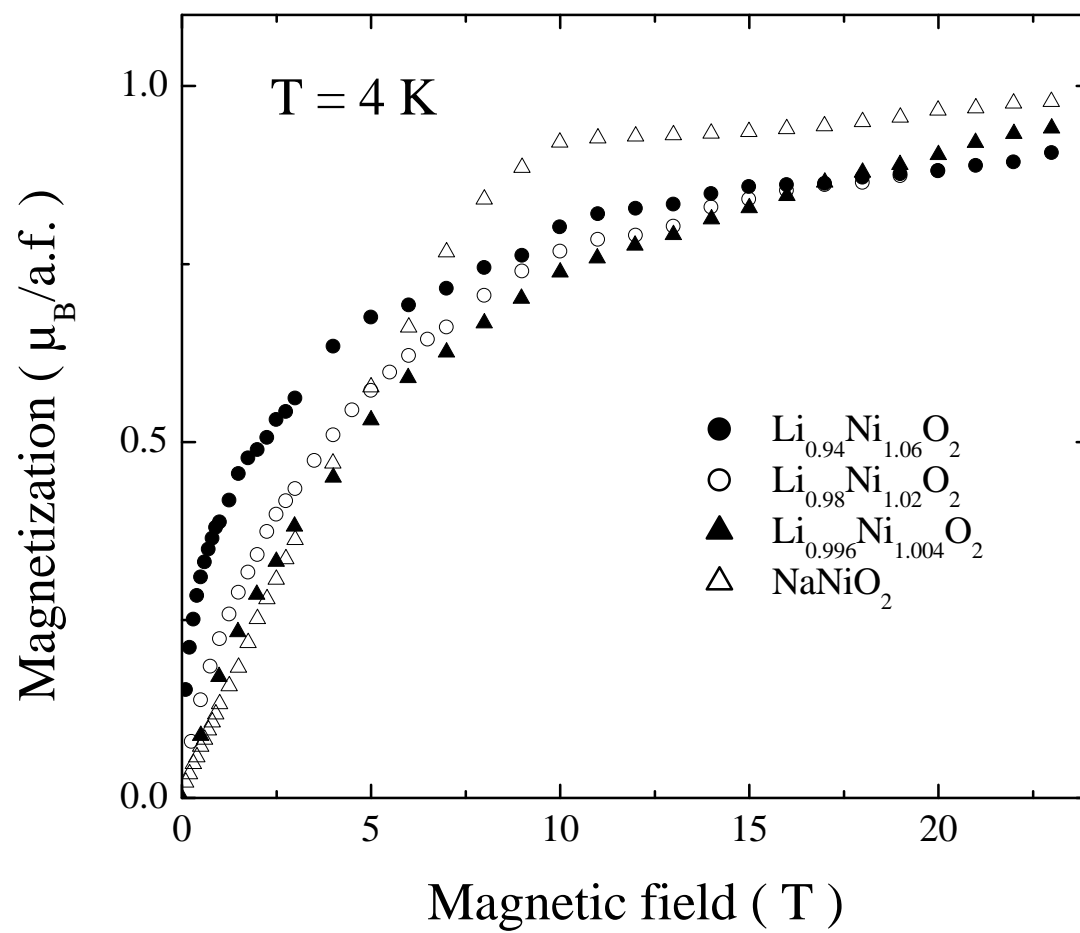
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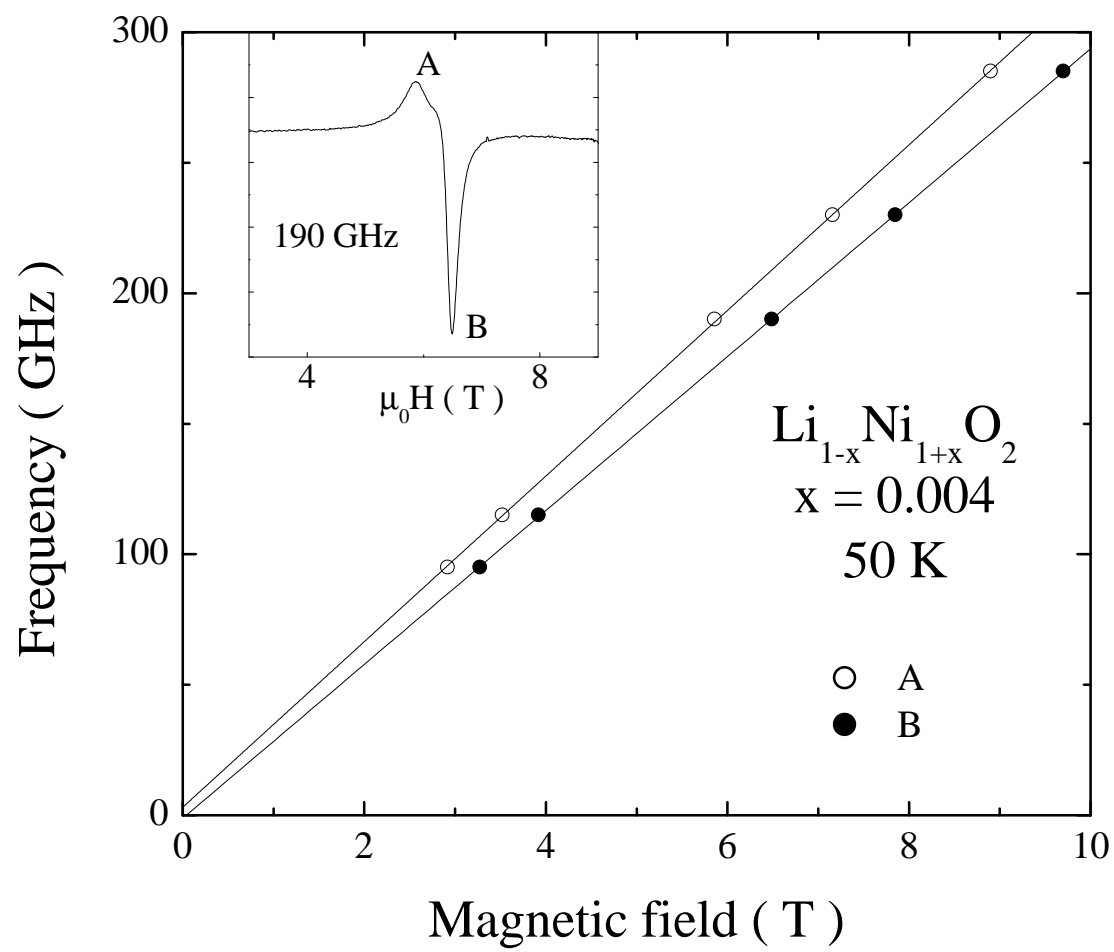
FIG. 4. High temperature ($T=200\text{K}$) frequency-field ESR diagrams for NaNiO_2 (dashed line) and $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, $x=0.004$ (continuous line). Insets : typical spectra for both samples.

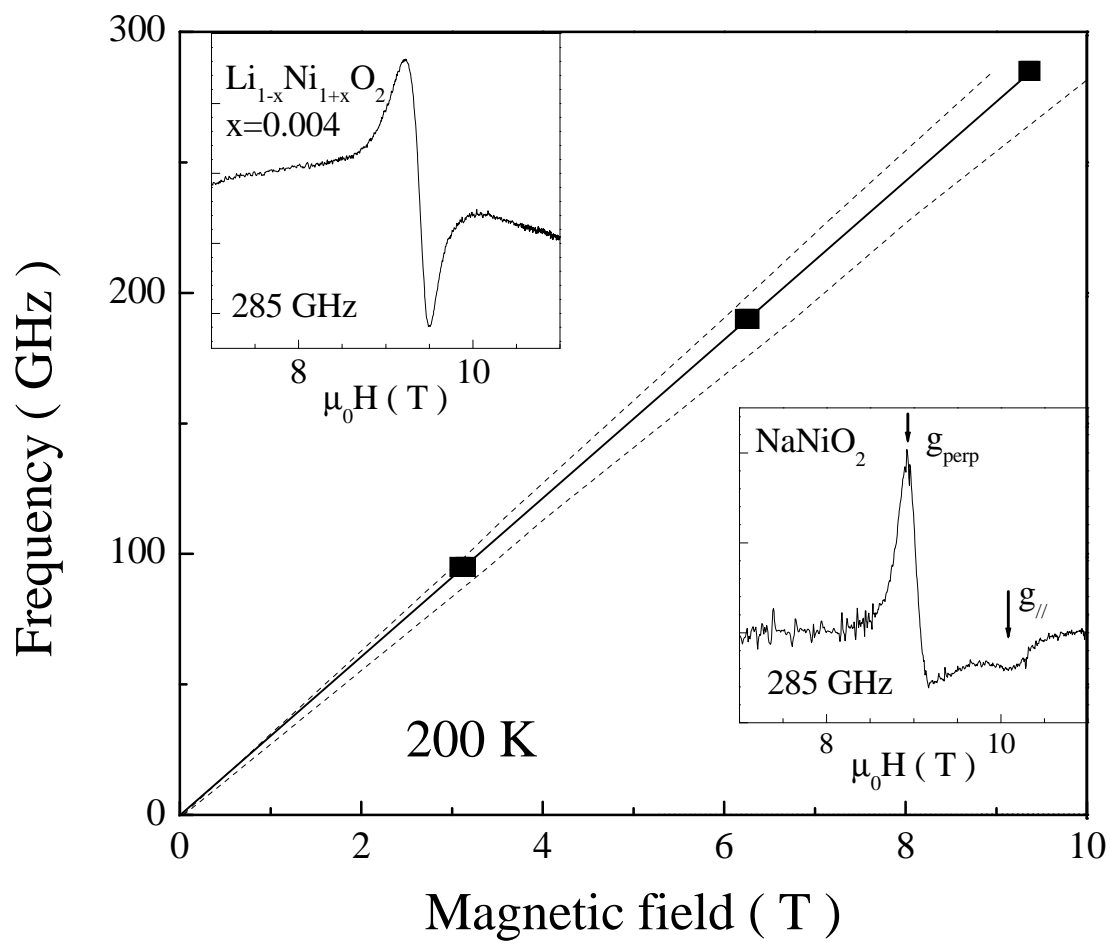
FIG. 5. Sketch of the magnetic frustration mechanism proposed here for quasi-stoichiometric $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$. The effective FM interplane coupling induced by extra Ni ions in the Li planes, hiddens the macroscopic magnetic ordering of NaNiO_2 , driven by the weak AF interplane interaction.

FIG. 3. From typical low temperature ESR spectra of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, $x=0.004$, showing two features A and B (see example in the inset), very similar to NaNiO_2 , the frequency-field diagram is proposed.









Ferrimagnetic cluster

